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Photoelectron Spectroscopy Group

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Research Activities

(I) SURFACE AND BULK CORE-LEVEL SHIFTS OF THE Si(111)$\sqrt{3}$x$\sqrt{3}$-Ag AND -Ga SURFACES[1,2]

(S. Kono, K. Higashiyama, T. Kinoshita, Y. Enta and F. Maeda)

a. Si2p and Ag4d photoelectron spectra have been measured for the Si(111) $\sqrt{3}$x$\sqrt{3}$-Ag surface at both surface- and bulk-sensitive photon energies. A dramatic shift of the bulk Si2p component for the $\sqrt{3}$x$\sqrt{3}$ surface has been observed and is attributed to the presence of an inherently charged $\sqrt{3}$x$\sqrt{3}$ layer. A single component of surface Si2p levels is found for the $\sqrt{3}$x$\sqrt{3}$ surface. Discussion of structural and growth models of the $\sqrt{3}$-Ag surface is made.

b. Surface and bulk sensitive Si2p and Ga3d photoelectron spectra have been measured for the Si(111)$\sqrt{3}$x$\sqrt{3}$-Ga surface. Only a single surface Si2p component and a single Ga3d component are found for the $\sqrt{3}$x$\sqrt{3}$-Ga surface from a nonlinear least-squares analysis. These findings are consistent with the threefold-hollow 1/3ML adatom models proposed for the $\sqrt{3}$x$\sqrt{3}$-Group III metal surfaces.

(II) INVERSE- AND DIRECT-PHOTOELECTRON SPECTROSCOPY STUDIES OF METAL-ADSORPTIONS ON Si(111) SURFACES[4,5]

(T. Kinoshita, Y. Enta, H. Ohta, S. Suzuki and S. Kono)

a. Momentum-resolved inverse photoemission spectra have been measured for Si(111)$\sqrt{3}$x$\sqrt{3}$-Sn and -In surfaces. An empty part of the metallic surface-state band for $\sqrt{3}$x$\sqrt{3}$-Sn is observed. It is noted that the metallic band (including the empty and filled parts) for the $\sqrt{3}$x$\sqrt{3}$-Sn surface disperses

in the same manner as the empty band for the $\sqrt{3}\times\sqrt{3}$-In surface. This is consistent with the previous proposal that the atomic arrangements of the $\sqrt{3}\times\sqrt{3}$-In and $\sqrt{3}\times\sqrt{3}$-column III surfaces are identical to each other. For the Si(111)$2\sqrt{3}\times2\sqrt{3}$-Sn surface, momentum-resolved inverse photoemission spectra and coverage-dependent angle-resolved photoemission spectra have been measured. It has been found that the $2\sqrt{3}\times2\sqrt{3}$-Sn surface is semiconducting and at least two filled- and one empty-surface-state bands exist in the bulk band gap.

b. Angle-resolved ultraviolet photoelectron spectra have been measured for the Si(111)$\sqrt{3}\times\sqrt{3}$-Bi surface. It has been found that at least four occupied surface-state bands exist on the $\sqrt{3}\times\sqrt{3}$-Bi surface. The results are compared particularly with the surface electronic structures of 1/3ML adatom models with the consideration of spin-orbit interaction.

(III)ATOMIC-GEOMETRY DETERMINATION OF METAL-ADSORBED Si(111) SURFACES BY PHOTOELECTRON DIFFRACTION[5,7]

(K. Higashiyama, C. Y. Park, T. Abukawa and S. Kono)

a. Azimuthal angle diffraction patterns of Sn3d X-ray photoelectrons and Sn MNN Auger electrons have been measured for the Si(111)$\sqrt{3}\times\sqrt{3}$-Sn surface. Kinematical calculations with spherical and plane wave formulae have been made to analyze the diffraction patterns. It is found that one third of a monolayer of Sn atoms form an overlayer with the vertical distance of more than $\sim$1Å above the substrate. Although the registry of the overlayer to the substrate is not determined by the present analysis, it is reasonable to consider that the T_4 or H_3 model, originally proposed for the Si(111) $\sqrt{3}\times\sqrt{3}$-Group III metal surfaces, is appropriate for the $\sqrt{3}\times\sqrt{3}$-Sn surface. The effect of double scattering calculations on diffraction patterns has been examined.

b. It is found by X-ray photoelectron spectroscopy and LEED that the saturation coverage of Bi is one monolayer for the Si(111)$\sqrt{3}\times\sqrt{3}$-Bi surface. Azimuthal dependence of Bi4d photoelectron diffraction has been measured for the Si(111) $\sqrt{3}\times\sqrt{3}$-Bi surface and analyzed kinematically. The results of the analysis have confirmed the presence of Bi-triplets with sides of 3.1Å as proposed by X-ray diffraction. It is further found that the Bi-triplets form an overlayer on the substrate.

c. Surface reconstructions of a submonolayer Sb/Si(111) system were investigated by low-energy electron diffraction and X-ray photoelectron spectroscopy. It has been found that the surface superstructures of diffuse 2x2 (or three-domain 2x1), $\sqrt{3}\times\sqrt{3}$, $5\sqrt{3}\times5\sqrt{3}$ and $7\sqrt{3}\times7\sqrt{3}$ are formed for the Sb coverages around one monolayer.

(IV)ELECTRONIC STRUCTURES OF ALKALI-ADSORBED Si(001)2x1 SURFACES[8]

(Y. Enta, T. Kinoshita, S. Suzuki and S. Kono)

a. Angle-resolved ultraviolet photoelectron spectra for the Si(001)2x1-K surface have been measured as a function of K coverage. It is found that the Si(001)2x1-K surface is semiconducting at saturation K coverage, in

contrast to previous interpretations of electron-energy-loss spectra based on a metallic Si(001)2x1-K surface. It is further inferred that the saturation coverage of K for the Si(001)2x1-K surface is one monolayer instead of half a monolayer as generally assumed for alkali-metal/Si(001) surfaces.

(V)ELECTRONIC STRUCTURE OF RHOMBOHEDRAL ARSENIC[11)]

(T.Takahashi, H. Ohsawa, N. Gunasekara, H. Ishii, T. Kinoshita and T. Sagawa)

Valence band structure of rhombohedral arsenic has been studied by angle-resolved photoemission using synchrotron radiation with photon energies between 20eV and 80eV. The experimentally determined band structures along the ΓT line and in the ΓLX and ΓWK planes were compared with the self-consistent pseudopotential band calculation performed in this study as well as with some representative band calculations presented so far.

(VI)UNOCCUPIED ELECTRONIC STRUCTURE OF GRAPHITE STUDIED BY ANGLE-RESOLVED SECONDARY-ELECTRON EMISSION AND INVERSE PHOTOEMISSION[12)]

(F. Maeda, T. Takahashi, H. Ohsawa and S. Suzuki)

Angle-resolved inverse photoemission spectroscopy (ARIPES) and angle-resolved secondary-electron emission spectroscopy (ARSEES) have been performed for graphite to establish experimentally the unoccupied-electronic-band structure as well as to study the difference between the two techniques. Remarkable differences have been found in the experimental two-dimensional band structures obtained by the two methods. The experimental results have been compared with the two different band calculations by R. C. Tatar and S. Rabii[Phys. Rev. B25, 4126(1982)]and by N. A. W. Holzwarth, S. G. Louie, and S. Rabii[Phys. Rev. B26, 5382(1982)]with special attention to the energy position of the three-dimensional interlayer band. The possible origin of the difference between ARIPES and ARSEES has also been discussed.

(VII)ELECTRONIC STRUCTURES OF GRAPHITE INTERCALATION COMPOUNDS[13-14)]

(T. Takahashi, N. Gunasekara, F. Maeda and T. Sagawa)

a. The electronic band structure of the first-stage cesium-intercalated graphite C_8Cs was determined by the highly-angle-resolved ultraviolet photoelectron spectroscopy. We found a prominent energy dispersion of the π^* band at $\bar{K}$ point for the first time. The experimentally-estimated electron occupancy of the π^* band is 0.45±0.05 unit electronic charge. This strongly suggests that another half of a unit electronic charge is accommodated in the interlayer band at the Γ point. The present experimental results have been compared with the theoretical band calculations presented so far as well as with the recently reported experimental results on Cs overlayer on graphite.

b. The electronic band structure of the first stage alkali-metal graphite intercalation compounds(C_8K, C_8Rb and C_8Cs) was determined by angle-resolved ultraviolet photoelectron spectroscopy. The dispersive feature of the π^* bands at $\bar{K}$ point in the Brillouin zone was clearly observed in all the

compounds. The electron occupancies in the π* band of C_8K, C_8Rb and C_8Cs were estimated to be 0.5±0.05 e (e;unit electronic charge), 0.45±0.05 e and 0.4±0.05 e, respectively. This strongly suggests that another half of the unit electronic charge is accommodated in the three-dimensional band at Γ point, which forms a spherical Fermi surface at the center of the Brillouin zone. The character of the three-dimensional band at Γ point was also discussed.

(VIII)ELECTRONIC STRUCTURES OF HIGH-Tc SUPERCONDUCTORS[15-19]

(T. Takahashi, F. Maeda and H. Arai)

a. Ultraviolet photoemission spectra of high-Tc superconductor $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ ($x=0.075$ and $\delta \leqq 0.04$) are presented. The experimental result was compared with the band calculations of La_2CuO_4 by Mattheiss and Takegahara et al. It was found that as regards the valence-band width (about 7eV) the experiment and the calculations are in good agreement with each other, but the position of the calculated valence bands contributed mainly by weakly bonding Cu(3d)-O(2p) states are shifted toward the lower binding energy by about 1eV with respect to the experiment. The possible origins for this discrepancy were discussed.

b. Electronic structure and chemical state of high-Tc superconductor $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ ($x=0.075$ and $\delta \leqq 0.04$) were studied by photoelectron spectroscopy. Resonant photoemission with synchrotron radiation showed that the copper atom in the La-Sr-Cu-O system is mostly divalent. The experimental results were compared with the band calculations performed for La_2CuO_4.

c. Photoelectron spectroscopy was performed for the high-Tc superconductors $LnBa_2Cu_3O_{7-\delta}$ (Ln=Y and Sm) with synchrotron radiation (SR) of 20-140eV as well as with the He I and Mg K_α lines. The valence band structure, the chemical states of component atoms (Cu and Sm), and the effect of the d-electron correlation were studied. Resonant photoemission with SR revealed that the electron correlation is relatively large (U_{dd}=5-6eV) and dominates the feature of the valence band structure.

d. Photoemission measurements have been performed on the high-Tc superconductor YBa_2-$Cu_3O_{6.85}$ using synchrotron radiation of 20-110eV. It is found that the valence band is shifted by 1.1 to 1.6eV towards higher binding energy relative to band calculations. The effective intra-atomic Coulomb energy between d-electrons (U_{dd}) was evaluated from the energy position of the valence-band satellite due to the two-hole bound state: U_{dd}=5-6eV, which is comparable to the valence-band width (W=6-7eV). This strongly suggests that electron correlation plays a key role in characterizing the electronic properties of this oxide superconductor.

e. Optical refrectance spectrum was measured for a single crystal $(La_{1-x}Sr_x)_2CuO_4$ in the energy range of 1-6eV.

(IX)GROWTH OF HIGH-Tc SINGLE CRYSTALS[20,21]

(T.Takahashi, copperated with H. Katayama-Yoshida, Y. Okabe and T. Suzuki in this department)

a. Large single crystals of high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$

(Tc∿90K) have been successfully grown in the cavity of bulk materials with a CuO flux. Crystals with a typical size of $2x2x0.3mm^3$ were obtained. As-grown single crystals do not show superconductivity at liquid nitrogen temperature. However, after annealing in O_2 flow for three days, they become superconductive at Tc∿90K.

b. An oxygen isotope effect is observed by a measurement of the resistivity when ^{16}O is substituted for ^{18}O in the $YBa_2Cu_3O_{7-\delta}$ compound. The superconducting transition temperature Tc is lowered by 0.4 K upon substitution. The results suggest that the phonon related to oxygen in the two-dimensional CuO_2 plane contributes to the mechanism of high-Tc superconductivity. When ^{63}Cu is substituted for ^{65}Cu, no appreciable isotope effect is observed.

Doctor Thesis(March 1988)

1) Electronic structures of submonolayer interfaces between column-III,IV and V metals, and Si(111) surfaces,studied by angle-resolved direct- and inverse-photoelectron spectroscopy.
Toyohiko Kinoshita

Master Thesis(March 1988)

1) Electronic structures of Si(001)2x1-K and -Cs surfaces studied by angle-resolved photoelectron spectroscopy.
Yoshiharu Enta

2) Unoccupied electronic structure of graphite studied by angle-resolved secondary electron spectroscopy.
Fumihiko Maeda

Pablications

1)Surface and bulk Core-Level Shifts of the Si(111)√3x√3-Ag Surface: Evidence for a Charged √3x√3 Layer,
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